

PYROLYSIS OF ORGANIC COMPOUNDS CONTAINING
LONG UNBRANCHED ALKYL GROUPS

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The Naval Research Laboratory has related the freezing point of JP-5 type fuels to the n-alkane content, specifically n-hexadecane (1). This relationship applies to jet fuels derived from any crude oil source. In general, jet fuels from shale crude have the highest and those from coal the lowest n-alkane content.

The quantity of large n-alkanes present in shale crude is insufficient to explain the alkane content (up to 37%) of fuels derived from shale. Precursors to small straight chain molecules in the jet fuel range might be long chain branched or cyclic substituted compounds which rupture during thermal refining processes. Attack on a side chain could afford a path to an alkane (2).

The thermal cracking of hydrocarbons is well documented in the literature (3-5). In 1933, Rice (6) proposed his classical free radical chain mechanism. The thermal decomposition of small alkanes (C_4-C_6) at low pressure and high temperature is now well understood. Similar radical mechanisms have been shown by several authors to account for the kinetics of the thermal decomposition of small (up to C_6) alkanes (7). Although a few examples of thermal cracking of higher hydrocarbons are found in the literature (8,9), they are not adequate for detailed comparison. Most of these studies have a particular emphasis on kinetics within the Rice-Kossiakoff theory parameters. Fabuss, Smith and Satterfield (8) have reported data and proposed a mechanism for n-hexadecane pyrolysis at pressures much higher than those studied by Rice.

The purpose of the present research is to test the validity of Fabuss-Smith-Satterfield (F-S-S) (8) for lower temperatures and higher pressures and to report the product distribution for the thermal cracking of large model compounds of varied structure. These compounds were pyrolyzed at temperature and pressure conditions typical of the petroleum refining process known as delayed coking.

EXPERIMENTAL

Reagents

1-Phenyl pentadecane, 1-phenyl tetradecane, 2-methyl octadecane, and tri-decyl cyclohexane obtained from Pfaltz and Bauer were passed through activated silica gel and fractionated. n-Hexadecane was a National Bureau of Standard reference sample and was used as received. 2-n-Pentadecyl pyridine was prepared by a standard method (10) and fractionated. The fraction boiling at 170°C at 33.2 Pa was retained and characterized by GC/MS. The

purity of the hydrocarbons was judged primarily from vapor phase chromatography. The area of the main chromatogram peak was always 99.9% when compared to a similar compound used as an internal standard.

Method

The compounds were pyrolyzed at temperature and pressure conditions typical of the petroleum refining process known as delayed coking. The conditions used were 723°K and about 600 kPa. A typical pyrolysis was carried out in a six inch long 1/4 inch o.d. 316 s.s. tube closed at one end and fitted at the other end with a stainless steel valve via a Swagelok fitting. The tube, containing a weighed amount of sample (approximately 0.1 g), was attached to a vacuum system, cooled to 195°K, and subjected to three freeze-pump-thaw cycles. The deaerated samples were warmed to room temperature and pyrolyzed by inserting them into 9/32 inch holes in a six inch diameter aluminum block fitted with heaters and a temperature controller. After the pyrolysis period, the tube was cooled to 195°K and the valve removed (unless the sample was analyzed for low-molecular weight gases). Benzene (or other appropriate solvent) was added to the tube which was then capped and warmed to room temperature. The solution and three subsequent rinses were transferred to a screw cap vial (teflon cap liner) and stored at 0°C until analysis. The sample concentration in the solvent was typically 5%. Prior to analysis, weighed amounts of internal standards were added. Since a typical chromatogram required 60 minutes, two internal standards were utilized. One (typically p-xylene) afforded quantitation for the peaks with short retention times and a second (typically 1-phenyl tridecane) was used for the peaks with longer retention times.

The stainless steel tubes were used for several runs. All tubes were subjected to the same cleaning procedure. They were filled with toluene, cleaned with a stainless steel brush, rinsed with toluene twice, then with methylene chloride and dried in air at 723°K for one hour.

The pyrolyzed samples were analyzed by three techniques, all based on gas chromatography. In the first, a Hewlett Packard Gas Chromatograph Model 5880A with F.I.D. detector equipped with a 50 meter wall-coated open tubular (OV-101) fused silica capillary column gave the necessary resolution to distinctly separate the alkanes and 1-alkenes. A carrier gas flow of one ml/minute was combined with an inlet split ratio of 60:1 and a 325°C injector temperature. The column temperature was programmed to 260°C at 4°/min after an initial hold at 50°C for 8 minutes. Peak identification for all three techniques was based on retention time matching with n-alkane and 1-alkene standards.

A second GC technique, used for longer retention time (C_{11} - C_{18}) n-alkanes and 1-alkenes, utilized a Perkin Elmer 3920B Gas Chromatograph equipped with an SE-30 110 foot support coated open tubular glass capillary column and a F.I.D. detector. The chromatogram was recorded and integrated on a Hewlett Packard Model 3390A reporting integrator. The temperature program was the same as for the 5880A analysis.

In the first technique, the long retention times coupled with an inlet split did not give reliable analytical response above C_{11} . The p-xylene internal standard was consequently used for C_8 - C_{10} analysis. The second GC technique was splitless and gave good response for longer retention times,

but not good separation at short retention times. The 1-phenyl tridecane internal standard was used for the C_{10} - C_{11} hydrocarbons. Both techniques gave the same analytical results for the mid-range carbon numbers (C_7 - C_{11}). This served as a sensitive check between the two techniques.

In the third technique, gases formed during pyrolysis were analyzed using a Beckman Model GC-72-5 gas chromatograph equipped with an Apiezon L alumina packed column and a F.I.D. In this mode, the column was operated at 200°C. The chromatogram was recorded and integrated on a Hewlett Packard Model 3390A reporting integrator. For this procedure, the tubes were cooled to 195°K after pyrolysis and the tube valve connected directly to a GC gas sampling valve via a swagelok connection. The sample tube was allowed to warm up to room temperature before analysis. An external standard was used for calibration. A pressure gauge measured the pressure in the sample loop at the time of analysis.

RESULTS

All samples were pyrolyzed at 723°K and 600 kPa in stainless steel tubes for time periods of 15, 30, 60, 120, and 180 minutes. There was no evidence of catalysis by the tube walls except for n-tridecyl cyclohexane. Only conditioned tubes (as described) were used.

Table I lists for each pyrolysis time, the sums of the n-alkanes and 1-alkenes for C_6 and higher aliphatics and the sums for all the substituted or branched hydrocarbons.

For 1-phenyl pentadecane, 1-phenyl tetradecane, and 2-n-pentadecyl pyridine, the sums of n-alkane and 1-alkene yields are nearly equal for a 60 minute pyrolysis. The effect of a 60 minute stress on straight chain hydrocarbon yield is illustrated in Figure 1 for 1-phenyl pentadecane and 2-n-pentadecyl pyridine. The n-alkane and 1-alkene for each carbon number is illustrated. Short pyrolysis times favor 1-alkenes while longer times favor increased n-alkane yields. The benzene substituted alkenes from both 1-phenyl pentadecane and 1-phenyl tetradecane are quite stable increasing from 3.6% and 2.6% for a 15 minute stress to 8.1% and 8.9% respectively for 180 minute stress. Styrene is the alkene present in highest yield. For 1-phenyl pentadecane, styrene varies from 0.7% at 15 minutes to 7.8% at 180 minutes and for 1-phenyl tetradecane from 0.5% at 15 minutes to 8.8% at 180 minutes.

Toluene and ethyl benzene were the most stable substituted benzenes formed. For a 15 minute pyrolysis of 1-phenyl pentadecane, 3.3% toluene and 2.9% ethyl benzene were formed. At 180 minutes, 14.9% and 0.2% respectively were formed. The same trend was noted for 1-phenyl tetradecane; at 15 minutes the toluene yield was 3.2% and ethyl benzene was 2.4%. At 180 minutes, 14.8% and 0.2% respectively were found. Ethyl benzene was a major initial product, but it does break down at long stress times. No benzene was found in the product mix. Figure 2 depicts the substituted alkane and alkene yield for each carbon number for a 60 minute pyrolysis of 1-phenyl pentadecane.

The pyridine substituted alkanes and alkenes from 2-n-pentadecyl pyridine show a remarkable dissimilarity with all of the other compounds pyrolyzed. The substituted alkenes exhibit very little thermal stability

after a pyrolysis of only 30 minutes and the very low yield drops to zero while the substituted alkane shows a high degree of stability gradually increasing in yield until at 180 minutes it attains 18.5%. The most stable of the substituted pyridines was 2-methyl pyridine which increased from 3.0% at 15 minutes to 11.7% at 180 minutes. No pyridine was found in the product mix.

Table II lists for the 60 minute pyrolysis, the total aliphatic product yield (C_1 and higher) for all of the compounds reacted. A comparison of Tables I and II gives the C_1 - C_4 yield from each of the long chain compounds. The yields are: 14.5% for 1-phenyl pentadecane, 13.1% for 1-phenyl tetradecane, 16.0% for 2-pentadecyl pyridine, 4.8% for n-hexadecane, 10.3% for 2-methyl octadecane, and 4.0% for n-tridecyl cyclohexane. That substituted pyridines and benzenes are much more susceptible to pyrolysis can be seen by a comparison with n-hexadecane. For a 15 minute pyrolysis 62.5% of the 1-phenyl pentadecane, 64.0% of 1-phenyl tetradecane and 53.5% of 2-n-pentadecyl pyridine remain, but 95.1% of the n-hexadecane remains. For a 60 minute pyrolysis, the C_1 - C_4 yield from n-hexadecane was only 4.8%. The same product trend is observed as for the other compounds; the n-alkane does not equal the 1-alkene yield until approximately the 120 minute pyrolysis of the n-hexadecane. At 180 minutes the n-alkanes predominate. Under the non-catalytic conditions of the experiment, isomerization was not expected and only slight traces of isomerization were found. At 180 minutes for the n-hexadecane, the lower n-alkanes and 1-alkenes predominate (n-pentane 9.6% and 1-pentene 5.0%). Figure 1 shows the decrease in the long chain compounds and the concomitant dramatic increase in the shorter chain hydrocarbons for the 60 minute pyrolysis of 1-phenylpentadecane and 2-n-pentadecyl pyridine.

The pyrolysis of 2-methyl octadecane proceeds at a faster rate than n-hexadecane. For a 15 minute pyrolysis, 77.1% of the 2-methyl octadecane remains versus 56.6% at 30 minutes. This compares to 95.1% and 75.9% respectively for the n-hexadecane. The straight chain hydrocarbons exceeded the branched hydrocarbons by 2 to 3 fold.

Substituted cyclohexanes would at first be expected to be considerably more reactive than straight chain hydrocarbons. This was not the case, however. For 15 minute pyrolysis, 87.3% of the n-tridecyl cyclohexane remains. The product distribution is as expected, but the n-alkane does not approximate the 1-alkene yield until 120 minutes of pyrolysis. The long chain cyclohexane also produced the lowest C_1 - C_4 yield (4.0%) for the 60 minute stress.

The substituted benzenes and pyridines did not yield either benzene or pyridine. However, n-tridecyl cyclohexane yielded cyclohexane as well as benzene, toluene, and methyl cyclohexenes in appreciable concentrations.

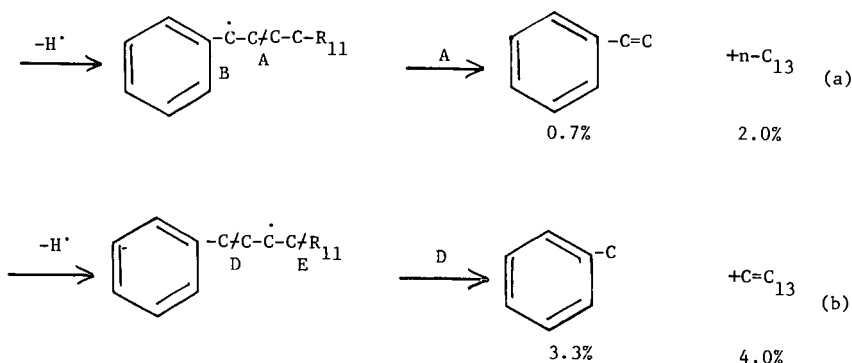
A material balance was run for each compound. The main peaks of the chromatograms account for approximately 85% of the original compounds. The very small peaks account for another 5-6%. It is also probable that the remainder is either polymerized or present as char. The formation of insolubles was not noticeable for short pyrolysis times. A small amount of insolubles was noted for the 120 and 180 minute pyrolysis times, especially for 2-pentadecyl pyridine. The product distribution was repeatable to 2% regardless of whether a new stainless steel tube or a previously used but conditioned tube was used.

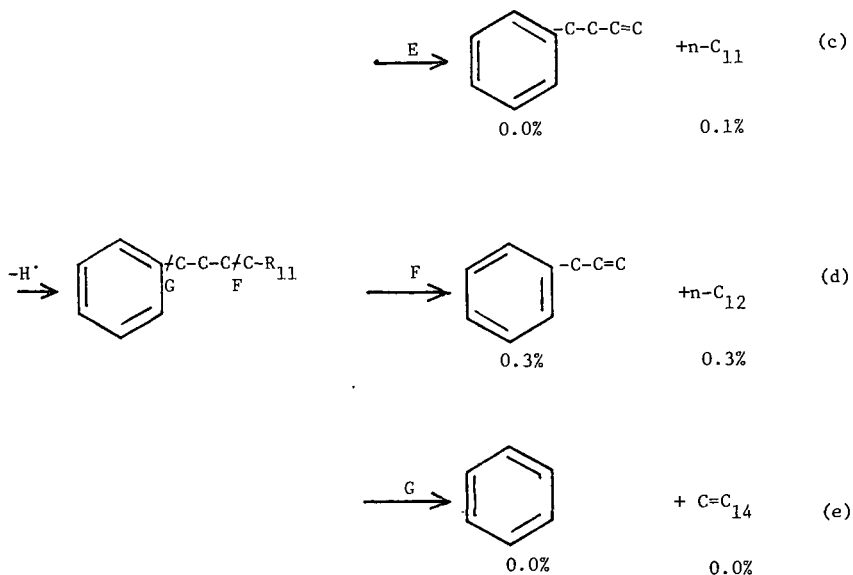
DISCUSSION

F-S-S behavior predictions are followed for all of the compounds pyrolyzed. The first members of the n-alkane and 1-olefin series are formed in smaller amounts than the second members. Low n-tetradecane (0%), n-pentadecane (0%) and 1-pentadecene (0.2%) yields for a 30 minute stress of n-hexadecane, follow traditional F-S-S theory. The model also predicts equal amounts of hydrocarbons in the intermediate chain length range, a behavior observed for several compounds in these experiments. For n-hexadecane, the total yield increases at 60 minutes but the shift to lower carbon number (C_8 - C_7) indicates product is forming and then undergoing secondary decomposition. The trend is extended significantly at longer times with C_8 alkane reaching 14.5% for the 180 minute stress of n-hexadecane.

The situation for aromatic substituted alkanes is different. Pyridine and benzene rings greatly enhance free radical formation. For example, the percent of 2-n-pentadecyl pyridine decomposed in 30 minutes is not matched by the n-hexadecane until almost 120 minutes. The total yield of hydrocarbon products at 30 minutes, 36.3% for 2-n-pentadecyl pyridine is not attained by n-hexadecane at 180 minutes. For a 15 minute stress, the C_8 - C_{12} yields for both 2-n-pentadecyl pyridine and 1-phenyl pentadecane are almost equal but a distinct C_{14} maxima is observed. The C_{11} compounds are also favored at short reaction times. The total yield increases at 30 and 60 minutes coupled with a steady decrease in C_{12} and C_{14} , compensated by a dramatic increase in C_8 - C_7 . The combined n-alkane + 1-alkene yield increased up to a 60 minute stress and then reversed. At 180 minute stress times, the n-alkane + 1-alkene sum approximates that of a 15 minute stress for both compounds (Table I). These trends indicate significant secondary decomposition at longer pyrolysis times.

A pyrolysis mechanism consistent with the observed product distribution can be pictured as follows for 1-phenyl pentadecane. The yield % for a 15 minute pyrolysis is shown below each compound. The same mechanism would apply for a long chain substituted pyridine.





Bond-scission reactions initiate (or are the first steps in) the mechanisms of the thermal pyrolysis of hydrocarbons.

The substituted benzenes produced in reactions a to e all thermally form via free radicals; alpha in step a, gamma in steps b-c, beta in steps d-e and on all other carbons of the alkane side chain. This is followed by beta-scission resulting in the product mix shown for steps a-e.

The free radical can be formed randomly on any carbon of the side chain as can be seen in the product breakdown. While most substituted benzenes are observed at short pyrolysis times, toluene predominates at all times indicating the gamma position is the most vulnerable to pyrolysis and that with increasing pyrolysis time secondary pyrolysis steps are of major importance.

The pyridine substituted alkenes are formed in considerable yield at short pyrolysis times, but after 30 minutes, the olefin concentration drops to zero. The pyridine substituent enhances the free radical breakdown of the olefin. This is not as dramatic for the benzene derivatives. The substituted olefins decrease, but only approach zero at 180 minutes of pyrolysis. As pyrolysis times increase, the substituted alkanes decrease in chain length with 2-methyl pyridine and 2-ethyl pyridine ultimately being the major products. With the substituted benzenes, toluene and styrene are the major products at longer pyrolysis times.

For 1-phenyl pentadecane, toluene increases from 3.3% at a 15 minute stress to 14.9% for a 180 minute stress. For 1-phenyl tetradecane, the toluene yield increases from 3.2% at 15 minutes to 14.8% for a 180 minute stress. The steady buildup of the toluene yield is reasonable since it has been found to be extremely resistant to pyrolysis at temperatures below 900°C (11). It is, however, quite reactive in the 1200-1500°C temperature range. These temperatures far exceed any in the present study. This thermal stability is not displayed by any of the other longer chain substituted benzenes.

For 2-n-pentadecyl pyridine, only two substituted pyridines (2-methyl and 2-ethyl) were found to be pyrolysis resistant at these experimental conditions.

The C_1 - C_4 product distribution was determined for the 60 minute pyrolysis only. This was the stress time at which the n-alkane + 1-alkene sum was maximized. Table II illustrates the C_1 and higher sum of the n-alkanes + 1-alkenes. The C_1 - C_4 yield was 16% for the substituted pyridines and approximately 14% for the substituted benzenes. The C_1 and C_2 yields are approximately equal (2-3%). The total n-alkane + 1-alkene yield percentage was 34.1% for 1-phenyl pentadecane, 37.9% for 2-n-pentadecyl pyridine, and 32.5% for 1-phenyl tetradecane.

2-Methyl octadecane was found to be significantly less reactive than the pyridine or benzene substituted alkanes. It is more reactive than the n-hexadecane. This is reasonable since the 2-methyl octadecane product distribution could be explained by the preferential attack on the tertiary hydrogen, the weakest C-H bond. The total product distribution (C_1 and up) was quite similar to the n-hexadecane.

Substituted cyclohexanes would be expected to be less reactive than either the pyridines or the benzenes. Surprisingly, it was also less reactive than n-hexadecane or 2-methyl octadecane at pyrolysis times of 60 minutes and less. The products other than the n-alkanes and 1-alkenes include toluene, benzene, and methyl cyclohexenes. The lower than expected conversion is due to self inhibition by the methyl cyclohexenes. Cyclohexene has been used by several authors as a free radical scavenger (12). At short pyrolysis times the methyl cyclohexene starts a steady buildup. As its concentration increases, aromatic compounds begin to appear. It would seem that these aromatic compounds are the secondary products which are formed from the decomposition of the substituted cyclohexenes. That toluene was the only substituted benzene formed was not surprising based on its stability and the observed toluene yield from the pyrolysis of the 1-phenyl pentadecane.

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TABLE I
Alkane and Alkene % Yield from Pyrolysis

Time (mins.)	1-Phenylpentadecane						1-Phenyltetradecane						2-Pentadecyl Pyridine					
	(Subst.)						(Subst.)						(Subst.)					
	n-Alkane	1-Alkene	Alkene	Alkene	Not Reacted		n-Alkane	1-Alkene	Alkene	Alkene	Not Reacted		n-Alkane	1-Alkene	Alkene	Alkene	Not Reacted	
15	4.2	10.1	8.0	3.6	62.5		2.7	8.0	7.1	2.6	64.0		5.2	7.6	6.1	2.7	53.5	
30	5.2	13.1	11.7	4.9	35.0		5.7	12.9	14.1	4.5	35.4		10.9	9.0	12.8	3.6	25.4	
60	9.3	10.3	20.9	4.4	8.7		9.0	10.4	19.6	5.7	7.2		11.0	10.9	15.5	0.1	12.0	
120	10.9	7.3	17.5	6.3	3.0		9.2	8.6	20.5	6.6	4.5		10.9	7.6	18.0	0.0	3.3	
180	9.3	3.8	18.4	8.1	1.0		9.5	3.4	17.9	8.9	1.4		6.7	2.6	18.5	0.0	0.1	

Time (mins.)	2-Methyl Octadecane						n-Tridecyl Cyclohexane						Hexadecane					
	(Branched)						(Subst.)						(Subst.)					
	n-Alkane	1-Alkene	Alkene	Alkene	Not Reacted		n-Alkane	1-Alkene	Alkene	Alkene	Not Reacted		n-Alkane	1-Alkene	Alkene	Alkene	Not Reacted	
15	0.6	1.3	0.7	0.1	77.1		0.1	0.1	0.6	0.1	87.3		0.2	1.9	95.1			
30	2.6	6.9	1.0	3.4	56.6		5.2	8.6	3.5	5.6	79.6		2.4	10.8	75.9			
60	7.8	12.4	2.2	6.0	34.9		5.3	10.7	3.6	6.1	42.0		10.3	17.6	33.6			
120	12.4	6.5	4.1	3.9	8.0		9.6	9.5	6.3	4.2	12.6		13.0	15.1	17.5			
180	6.8	6.6	3.0	1.7	4.7		9.3	5.1	6.1	2.5	3.7		22.0	10.6	5.7			

TABLE II
Total n-Alkane and 1-Alkene * % Yields for a 60 Minute Pyrolysis

	<u>1-Phenyl Pentadecane</u>	<u>1-Phenyl Tetradecane</u>	<u>2-Pentadecyl Pyridine</u>
n-Alkane	16.4	15.9	20.0
1-Alkene	17.7	16.6	17.9
TOTAL	34.1	32.5	37.9

	<u>Hexadecane</u>	<u>2-Methyl Octadecane</u>	<u>n-Tridecyl Cyclohexane</u>
n-Alkane	13.2	13.3	7.7
1-Alkene	19.5	17.2	12.3
TOTAL	32.7	30.5	20.0

* Unsubstituted only (C₁ and higher)

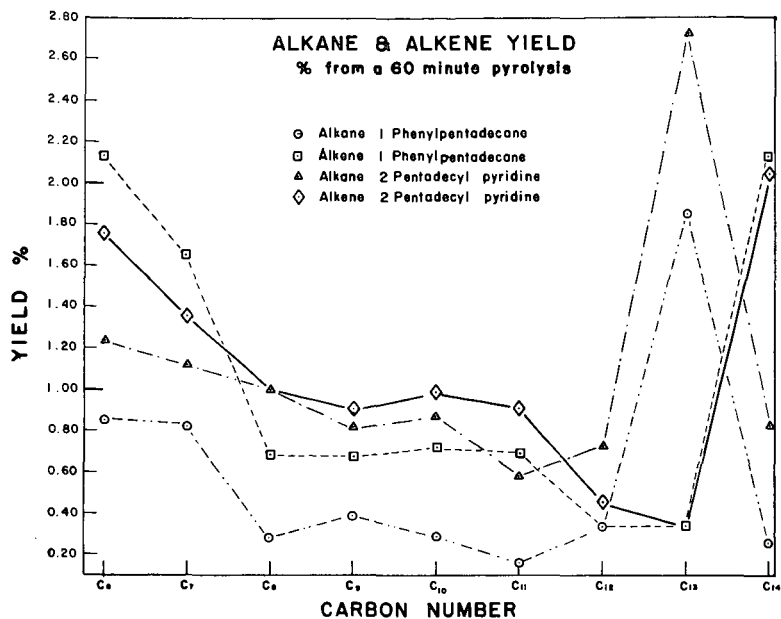


FIGURE 1.

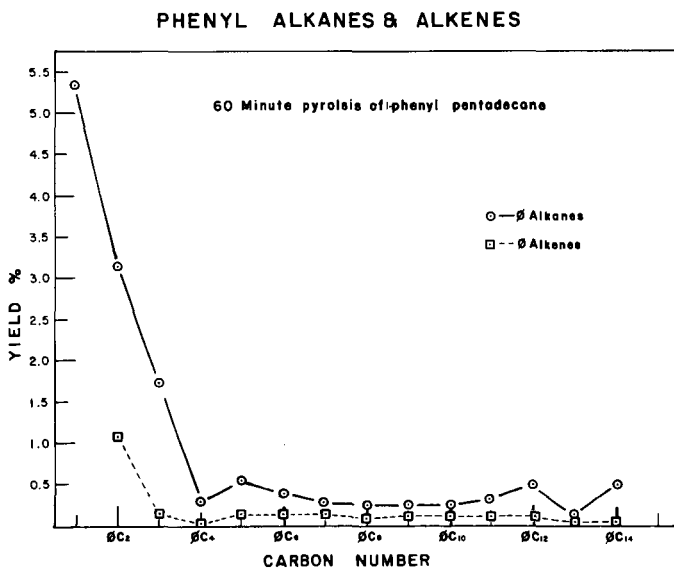


FIGURE 2.

Petrochemicals from Oil Shale
Via One-Step Pyrolysis

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Introduction

In the search for alternative feedstocks for the production of petrochemicals, oil shale emerged as an important candidate. The large deposits of oil shale in Colorado seem to be well suited to the manufacture of light aliphatics since its organic H/C (atomic) ratio is relatively high (1.5-1.6) and its kerogen is rich in aliphatic components (70-80%).

The two major routes to convert oil shale into petrochemicals are shown in Figure 1. For the one-step pyrolysis the most extensive previous studies were carried out by researchers at the Bureau of Mines in the fifties (1-5). Their work focused on gasoline manufacture but they also measured the yields of light hydrocarbons. Other sources also indicated the generation of ethylene via short residence time pyrolysis (6) and employing oxidative pyrolysis (7).

Two-step pyrolysis received far more attention than the one-step because it relies heavily on conventional, crude oil based technologies (8,9). The potential of this method for the petrochemical industry is well documented in recent publications (10-12). We decided to undertake a study of the one-step pyrolysis since we felt that it was lacking a fresh, systematic investigation and we wanted to evaluate its economic potential.

Experimental

For the experimental study Anvil Point III oil shale was selected. Some of its pertinent analytical data are presented in Table 1.

The experiments were conducted in a laboratory pyrolysis apparatus which was designed for total mass capture (Figure 2).

In a typical run the pulverized oil shale (120--140 mesh) was fed from a screw feeder, mixed with the carrier gas (nitrogen or carbon dioxide), and passed through the pyrolysis zone. Spent shale and tars were separated from the gases and the gas was collected in a burette by water displacement. At the end of the run the gas was pressure equalized and sampled for analysis. Since some fraction of the gas, even after purging the lines, did not reach the burette, samples were also taken at the solid/gas separator. The yields were calculated by combining these two analyses.